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Method for the Preparation of Diamond, Graphite or Their Mixture

Field of Technology

The present invention relates to a process for preparing diamond, graphite or mixtures of diamond and graphite from CO or CO_2 served as the carbon source by reduction with active metals.

Background of Technology

Diamond has the advantages of high melting point, low compressibility coefficient, high symmetry and high refractive index. It has wide applications in industrial manufacture and scientific research. Owing to the specific properties and uses thereof, quite long ago, people tried to prepare it by chemical method in order to supplement the insufficiency of the natural storage. A large amount of time and a long course of events have been spent on solving a series of problems such as the exploration of transition condition and relevant facilities as well as searches for an effective catalyst. In 1954, first work on successful preparation of diamond by conversion of graphite under strict control of high temperature and high pressure with FeS used as the flux was reported in Nature, Vol. 176, 51. Thereafter research and production of man-made diamond have been developing rapidly and grows to be a new industry. The conventional method of preparation for diamond involves the use of graphite as the raw material, molten metals (Ni, Cr, Mn, Fe, Co, Ti, Al etc) as the catalyst and flux, little diamond particles as crystal seeds. Thus graphite is converted into diamond under pressure of 5 – 100 kbar and high temperature of 1200 – 2400K. This kind of method has to endure critical conditions and very high cost.

Chinese patent 97119450.5 and Science, 1998, Vol. 281, 246 disclosed a method in which CCl_4 was used as the carbon source, Na was used as the reducing agent and solvent, Ni-Co metal was used as the catalyst. CCl_4 could be converted into diamond at 700℃. The size of the diamond particles thus prepared was less than 0.2 micrometer and the method had the danger of explosion. Therefore at the moment, the method is not suitable for large-scale industrial production of diamond.

On the other side, the global storage of CO_2 on earth is extremely abundant. CO_2 is also the by-product of exhaust emission of many industrial manufactures. When CO_2 is expelled into air, "greenhouse effect" will be induced which will cause the global weather getting warmer. As a result, many countries in the world have to spend huge amount of manpower and resources to bring it under control. CO_2 is non-toxic and cheap. Utilization of CO_2 as main raw material for synthesizing inorganic and organic compounds is one of the objectives of chemists. It is regrettable to notice that up to now no any well-industrialized method of treatment that uses CO_2 as raw material in huge amount has been reported.

Content of Technology

The objective of the present invention is to provide a method for the preparation of diamond, graphite or mixtures of diamond and graphite by using CO_2 (or compound that could release CO_2 on decomposition) or CO (or CO source) as the carbon source and active metals as the reducing agents.

In order to realize the above-mentioned objective, the inventor of present invention

carried out a large amount of intensive investigations and found that CO_2 or CO_2 source and CO or CO source could react with active metal that is capable of reducing them into elementary carbon to form diamond, graphite or mixture of diamond and graphite.

Hence the present invention provides a method for preparing diamond, graphite or mixture of diamond and graphite. The method includes the steps in which active metals (capable of reducing carbon source into elementary carbon) under reducing conditions capable of reducing carbon source into elementary carbon are brought in contact with carbon source (CO and/or CO source and/or CO_2 and/or CO_2 source) to start a reduction reaction. The carbon source is preferably CO_2 and/or CO_2 source.

In the method of the present invention based on a preferred approach, CO_2 is used as the carbon source and is reduced by active metal to form diamond. Therefore any compound, such as dry ice, oxalates, carbonates or their mixture that could release CO_2 on decomposition as well as CO_2 itself could be used as a carbon source to prepare diamond.

Any metal that is capable of reducing CO or CO_2 into elementary carbon could be used as an active metal in the present invention. Metals whose standard electrode potentials are lower than -2.2 V are preferred. Such metals include (but not limited to) one or mixture of several of the following: metal Na, Li, K, Rb, Cs, or Mg, Ca, Sr, Ba. Although not wished to be bound by any theory, it is generally believed that standard electrode potential of CO_2 / $CO_2^{\cdot -}$ in aprotic solvent is -2.2 V. $CO_2^{\cdot -}$ is an active single electron free radical that reacts easily with CO_2 to form C—C linkage. Therefore those metals having standard electrode potential lower than -2.2 V, such as the standard electrode potential of Na is -2.7 V, the standard electrode potential of K is -2.931 V, the standard electrode potential of Li is -3.04 V, the standard electrode potential of Mg is -2.37 V, could all be used to reduce CO_2 to prepare diamond or mixtures of diamond and graphite.

Temperature of reduction reaction suitable to be used in the present invention is preferably 300℃ at least, preferably 300 - 2000℃. Specific temperature of reaction to be adopted would depend on the selected pressure condition and the selected active metal used. When metal Na or Li, K, Rb, Cs is used as reducing metal, reaction temperature is preferably 300℃ at least, more preferably 300 - 2000℃; When Mg, Ca, Sr, Ba is used as reducing metal, reaction temperature is preferably 650℃ at least, more preferably 650 - 2000℃;

Pressure of reduction reaction suitable to be used in the present invention is 0.2 kbar at least, preferably 0.2 -5.0 kbar. Specific pressure of reaction to be adopted would depend on what kind of elementary carbon product expected to be prepared and on the temperature selected. It should be emphasized that when diamond of high purity is expected to be synthesized, higher pressure is preferably adopted, more preferably higher pressure is maintained throughout the whole course of reaction.

Under higher pressure, the product obtained is diamond with high density; If the reaction is carried out in a reaction kettle that could not maintain higher pressure automatically, pressure of the system will drop in the course of reaction and the main product formed at that time will be graphite of lower density and the final product will be a mixture of graphite and diamond. Under higher temperature and higher pressure, said reaction route is as follows;

$3CO_2 + 4M = C$ (diamond, graphite or mixture of graphite and diamond) $+ 2M_2CO_3$ (M = Li or Na, K, Rb, Cs)

$3CO_2 + 2N = C$ (diamond, graphite or mixture of graphite and diamond) $+ 2NCO_3$ (N = Mg or Ca, Sr, Ba)

The thermodynamic property of diamond determines that a definite pressure is necessary for the formation of diamond. The higher the pressure is, the more favorable the formation of diamond will be. In the method of the present invention, it is possible to vary the pressure of the reaction system by controlling the amounts of dry ice, oxalate, carbonate or CO_2 gas added. Experiments prove that when temperature is lower than 300℃ and pressure is lower than 0.2 kbar, no diamond will be formed. Judging the tolerance of the common reaction kettle, it is appropriate to carry out the reaction at a temperature of 300 - 2000℃ and a pressure of 0.2 – 5.0 kbar.

Reduction reaction of the present invention is preferably carried out under a supercritical condition. It is believed that when CO_2 is heated to exceed its critical point (for example, 31.5℃, 73 kbar), its gas phase and liquid phase will turn into a single supercritical phase having high mixing rate and relatively weaker intermolecular association power. This will induce the supercritical CO_2 to possess high reactivity. Many physico-chemical properties of the supercritical CO_2 lie between gas and liquid and possess the advantages of both two. For instance, it possesses dissolution power and heat conductivity coefficient similar to liquid and viscosity coefficient and diffusion coefficient similar to gas. In the preferred approach of the present invention, temperature and pressure are adjusted to turn the CO_2 of the reaction system into supercritical state.

Based on the method of the present invention, time of the reduction reaction is determined by temperature, pressure and reducing power of the reducing metal adopted. 10 – 48 hours are preferred.

After the completion of the reaction, the reaction system is cooled to room temperature, and pressure is lowered to atmospheric pressure and diamond, graphite or their mixture could be obtained.

If small diamond granule, such as 300 μ m-sized diamond granule, is added to the above-mentioned reaction system as a crystal seed, up to 6000 μ m-sized diamond granule could be obtained. For the sake of convenience and lowering cost, reaction product of the preceding experiment is preferably selected as the crystal seed.

In order to obtain pure diamond, diamond or mixture of diamond and graphite obtained by the method of the present invention could be purified by any conventional purification method. For instance, it is possible to obtain pure diamond particulate through intensive heat treatment with perchloric acid or sedimentation separation with 0.5% aqueous solution of gum Arabic.

If only graphite is to be prepared, reaction could be carried out merely at pressure lower than 0.2 kbar.

The present invention utilizes industrial by-product CO_2 or CO or compounds capable of releasing CO or CO_2 on decomposition as the main raw material and thus possesses the advantages of low reaction temperature, good dispersion and good flowability of carbon source. Diamond crystals obtained have good crystallinity, contains no impurities and could have size up to several hundred micrometers. If small diamond granule, such as 300 μ m-sized diamond granule, is added to the above-mentioned reaction system as a crystal seed, diamond granule with size of 3000 μ m or even up to 6000 μ m could be obtained.

Especially when CO_2 is used as the carbon source, the approach has the following advantages: CO_2 is the by-product of exhaust emission of many industrial manufactures. When CO_2 is expelled into air, "greenhouse effect" will be induced which will cause the global weather getting warmer. As a result, many countries in the world have to spend huge amount of manpower and resources to bring it under control. The present invention uses CO_2 as the raw material to prepare diamond, graphite or their mixture. Thus this approach not only could turn wastes into valuables and could perform it at low cost but also it is beneficial to the improvement of environment and thus possesses good social benefit and economic benefit. The present invention could also be used to reduce CO_2 into graphite that is also an important industrial raw material. Using CO_2 as a reactant has advantages of non-toxicity, non-combustion and safe handling. In addition, CO_2 could easily be separated from the reactant and thus by lowering the pressure, CO_2 turns into gas and then is expelled and the final product could conveniently and directly be obtained.

In comparison with the conventional method of preparation for diamond, the present method uses lower temperature, pressure, simpler facility and is of low cost and easily manipulative. When compared with method of reduction of CCl_4 into diamond, the present method is safer in manipulation, could yield diamond of larger size and thus possesses significance of practical industrial production and potential wide markets.

Brief Description of the Drawing

Figure 1 is the X-ray diffraction profile for the sample obtained in Example 1.

Figure 2 is the Raman spectrum for the sample obtained in Example 1.

Figure 3a, 3b are SEM (scanning electronic micrograph) profiles for the diamond sample obtained in Example 1. Figure 3b is a magnified profile for the portion selected by the square in Figure 3a.

Detailed Description of the Preferred Embodiments

Example 1:

2.0 g of metal sodium of chemical pure grade and 8.0 g of self-prepared dry ice were put into an autoclave of a capacity of 12 mL. The autoclave was heated to 440℃ so that the pressure in the autoclave reached 500 – 1000 kbar and this state was maintained for 16 hrs. Then the autoclave was cooled to room temperature and the pressure in the autoclave dropped to atmospheric pressure. The reaction product was treated with HCl and washed with water. 0.20 g of black powder was obtained.

The X-ray diffraction spectrum of the sample was measured. In the diffraction spectrum (Fig. 1) of the sample obtained, there appeared 3 characteristic diffraction peaks of cubic phase diamond (JCPDS card No. 6-675) and 1 rather broad diffraction peak of graphite at 26.2° .

Raman spectrum of the sample was measured. In the spectrum, there was a characteristic peak of diamond at 1332 cm^{-1} (Fig. 2, 1332 cm^{-1} is the characteristic peak of diamond, see Nature 1999, Vol. 402, 164) with its half-height width of 4.7cm^{-1} close to that of natural diamond (2.5 cm^{-1}), which indicating that the diamond synthesized has good crystallinity. In addition there were two characteristic peaks of graphite at 1363 cm^{-1} and 1591 cm^{-1} respectively indicating that the product was a mixture of diamond and graphite.

The mixed powder obtained was intensively heat-treated with perchloric acid at 160℃

and 0. 018 g of pure diamond granule was finally obtained. SEM micrograph indicated that the average diameter of the diamond granule was 100 μ m (Figure 3).

If the metal sodium of the present example was replaced by Li, K, Rb, Cs as the reducing metal, mixtures of diamond and graphite were similarly obtained.

Example 2:

2.5 g of potassium of chemical pure grade was put into an autoclave. Said autoclave was heated to 470℃ and CO_2 gas was fed into an autoclave under pressure to 400 – 1500 kbar and this state was maintained for 12 hrs. Then the autoclave was cooled to room temperature and the pressure in the autoclave dropped to atmospheric pressure. The reaction product was treated with HCl and washed with water. 0.22 g of black powder was obtained.

X-ray diffraction pattern and Raman spectrum of the sample were measured and the obtained sample was proved to be a mixture of diamond and graphite.

The mixed powder obtained was separated by sedimentation in 0.5% aqueous solution of gum Arabic and 0. 02 g of pure diamond granule was finally obtained. SEM micrograph indicated that the average diameter of the diamond granule was 120 μ m and the maximum diameter could reach 300 μ m.

If potassium of the present example was replaced by Li, Na, Rb, Cs as the reducing metal, mixture of diamond and graphite was similarly obtained.

Example 3:

2.2 g of potassium of chemical pure grade and 6.0 g of $MgCO_3$ were put into an autoclave of 12 mL that was heated to 500℃ and to a pressure of 800 – 2000 kbar and this state was maintained for 18 hrs. Then the autoclave was cooled to room temperature and the pressure in the autoclave dropped to atmospheric pressure. 0.08 g of black powder was obtained.

X-ray diffraction pattern and Raman spectrum of the sample were measured and the obtained sample was proved to be a mixture of diamond and graphite.

The mixed powder obtained was intensively heat treated with perchloric acid and pure diamond granule with average diameter of the diamond granule of 260 μ m (determined by SEM) was obtained.

If potassium of the present example was replaced by Li, Na, Rb, Cs as the reducing metal, mixtures of diamond and graphite were similarly obtained.

If $MgCO_3$ of the present example was replaced by Ag_2CO_3, $CaCO_3$, $CdCO_3$, $CoCO_3$, $CuCO_3$,$FeCO_3$, $BaCO_3$, $MnCO_3$, $NiCO_3$, $PbCO_3$, $SrCO_3$, $ZnCO_3$, Na_2CO_3, K_2CO_3, Li_2CO_3 and the temperature was changed to 470℃, 950℃, 500℃, 450℃, 480℃, 520℃, 1000℃, 460℃, 550℃, 540℃, 900℃, 440℃, 1500℃, 1400℃, 750℃ respectively, a mixture of diamond and graphite was similarly obtained.

Example 4:

2.2 g of Li of chemical pure grade and 14.0 g of NiC_2O_4 were put into an autoclave of 12 mL which was heated to 560℃ and to a pressure of 500 – 1000 kbar and this state was maintained for 12 hrs. Then the autoclave was cooled to room temperature and the pressure in the autoclave dropped to atmospheric pressure. The reaction product was treated with HCl and washed with water. 0.28 g of black powder was obtained.

X-ray diffraction pattern and Raman spectrum of the sample were measured and the obtained sample was proved to be a mixture of diamond and graphite.

The mixed powder obtained was intensively heat treated with perchloric acid at 160℃ and pure diamond granule with average diameter of the diamond granule of 100 μ m (determined by SEM) was obtained.

If Li of the present example was replaced by K, Na, Rb, Cs as the reducing metal, a mixture of diamond and graphite was similarly obtained.

If NiC_2O_4 of the present example was replaced by CaC_2O_4, CdC_2O_4, CoC_2O_4, CuC_2O_4, CrC_2O_4, FeC_2O_4, $K_2C_2O_4$, MnC_2O_4, $La_2(C_2O_4)_3$, $Li_2C_2O_4$, MgC_2O_4, $Na_2C_2O_4$, PbC_2O_4, SrC_2O_4, ZnC_2O_4, $La_2(C_2O_4)_3$, $Cr_2(C_2O_4)_3$, a mixture of diamond and graphite was similarly obtained.

Example 5:

2.5 g of Mg of chemical pure grade was put into an autoclave of 12 mL. The autoclave was heated to 650℃ and CO_2 gas was fed into an autoclave under pressure to 500 – 1500 kbar and this state was maintained for 12 hrs. Then the autoclave was cooled to room temperature and the pressure in the autoclave dropped to atmospheric pressure. The reaction product was treated with HCl and washed with water. 0.23 g of black powder was obtained.

X-ray diffraction pattern and Raman spectrum of the sample were measured and the obtained sample was proved to be a mixture of diamond and graphite.

The mixed powder obtained was intensively heat treated with perchloric acid and a pure diamond granule was finally obtained. SEM micrograph indicated that the average diameter of the diamond granule was 60 μ m.

If Mg of the present example was replaced by Ca, Sr, Ba as the reducing metal and temperature was changed to 850℃, 800℃ and 750℃ respectively, mixture of diamond and graphite was similarly obtained.

Example 6:

2.5 g of Ca of chemical pure grade and 8.0 g of self-prepared dry ice were put into an autoclave of capacity of 12 mL. The autoclave was heated to 850℃ so that the pressure in the autoclave reached 500 – 1000 kbar and this state was maintained for 16 hrs. Then the autoclave was cooled to room temperature and the pressure in the autoclave dropped to atmospheric pressure. The reaction product was treated with HCl and washed with water. 0.20 g of black powder was obtained.

X-ray diffraction pattern and Raman spectrum of the sample were measured and the obtained sample was proved to be a mixture of diamond and graphite.

The mixed powder obtained was intensively heat treated with perchloric acid and pure diamond granule was finally obtained. SEM micrograph indicated that the average diameter of the diamond granule was 130 μ m.

If Mg of the present example was replaced by Ca, Sr, Ba as the reducing metal and temperature was changed to 850℃, 800℃ and 750℃ respectively, mixture of diamond and graphite was similarly obtained.

Example 7:

2.0 g of Mg of chemical pure grade and 14.0 g of CoC_2O_4 were put into an autoclave

of 12 mL which was heated to 650℃ and to a pressure of 500 – 1000 kbar and this state was maintained for 16 hrs. Then the autoclave was cooled to room temperature and the pressure in the autoclave dropped to atmospheric pressure. The reaction product was treated with HCl and washed with water. 0.20 g of black powder was obtained.

X-ray diffraction pattern and Raman spectrum of the sample were measured and the obtained sample was proved to be a mixture of diamond and graphite.

The mixed powder obtained was intensively heat treated with perchloric acid and pure diamond granule with average diameter of the diamond granule of 50 μ m (determined by SEM) was obtained.

If Mg of the present example was replaced by Ca, Sr, Ba as the reducing metal and the temperature was changed to 850℃, 750℃, 800℃, mixture of diamond and graphite was similarly obtained.

If CoC_2O_4 of the present example was replaced by CaC_2O_4, CdC_2O_4, NiC_2O_4, CuC_2O_4, CrC_2O_4, FeC_2O_4, $K_2C_2O_4$, MnC_2O_4, $La_2(C_2O_4)_3$, $Li_2C_2O_4$, MgC_2O_4, $Na_2C_2O_4$, PbC_2O_4, SrC_2O_4, ZnC_2O_4, mixture of diamond and graphite was similarly obtained.

Example 8:

3.5 g of Sr of chemical pure grade and 16.0 g of $FeCO_3$ were put into an autoclave of 12 mL which was heated to 800℃ and to a pressure of 500 – 1500 kbar and this state was maintained for 16 hrs. Then the autoclave was cooled to room temperature and the pressure in the autoclave dropped to atmospheric pressure. The reaction product was treated with HCl and washed with water. 0.28 g of black powder was obtained.

X-ray diffraction pattern and Raman spectrum of the sample were measured and the obtained sample was proved to be a mixture of diamond and graphite.

The mixed powder obtained was intensively heat treated with perchloric acid and pure diamond granule with average diameter of the diamond granule of 100 μ m (determined by SEM) was obtained.

If Sr of the present example was replaced by Ca, Mg, Ba as the reducing metal and the temperature was changed to 850℃, 650℃, 800℃, mixture of diamond and graphite was similarly obtained.

If $FeCO_3$ of the present example was replaced by $CaCO_3$, $CdCO_3$, $CoCO_3$, $CuCO_3$, Mg CO_3, $BaCO_3$, $MnCO_3$, $NiCO_3$, $PbCO_3$, $SrCO_3$, $ZnCO_3$, Na_2CO_3, K_2CO_3, Li_2CO_3 and the temperature was changed to 950℃, 820℃, 840℃, 880℃, 860℃, 1000℃, 860℃, 850℃, 840℃, 900℃, 940℃, 1500℃, 1400℃, 850℃, mixture of diamond and graphite was similarly obtained.

Example 9:

2.2 g of K of chemical pure grade was put into an autoclave and a diamond seed of size of 300 μ m was added. The autoclave was heated to 520℃ and CO_2 gas was fed into autoclave under pressure to 500 – 1500 kbar and this state was maintained for 16 hrs. Then the autoclave was cooled to room temperature and the pressure in the autoclave dropped to atmospheric pressure. The reaction product was treated with HCl and washed with water. 0.24 g of black powder was obtained.

X-ray diffraction pattern and Raman spectrum of the sample were measured and the obtained sample was proved to be a mixture of diamond and graphite.

The mixed powder obtained was intensively heat treated with perchloric acid and a pure diamond granule was finally obtained. SEM micrograph indicated that the average diameter of the diamond granule was 430 μ m.

If K of the present example was replaced by Li, Na, Rb, Cs as the reducing metal, mixture of diamond and graphite was similarly obtained.

Example 10:

3.2 g of Cs of chemical pure grade and 8.0 g of self-prepared dry ice were put into an autoclave of a capacity of 12 mL and a diamond seed of 300 μ m was also added. After the autoclave was heated to 300℃, CO_2 gas was fed under pressure, so that the pressure in the autoclave reached 200 – 1500 kbar and this state was maintained for 16 hrs. Then the autoclave was cooled to room temperature and the pressure in the autoclave dropped to atmospheric pressure. The reaction product was treated with HCl and washed with water. 0.12 g of black powder was obtained.

X-ray diffraction pattern and Raman spectrum of the sample were measured and the obtained sample was proved to be a mixture of diamond and graphite.

The mixed powder obtained was intensively heat treated with perchloric acid and a pure diamond granule was finally obtained. SEM micrograph indicated that the average diameter of the diamond granule was 300 μ m.

If Cs of the present example was replaced by Li, Na, Rb, K as the reducing metal and temperature was changed to 450℃, 520℃, 480℃ and 580℃ respectively, mixture of diamond and graphite was similarly obtained.

Example 11:

2.2 g of potassium of chemical pure grade, 6.0 g of $MgCO_3$ and diamond seed of 300 μ m were put into an autoclave of 12 mL which was heated to 500℃ and to a pressure of 800 – 1000 kbar and this state was maintained for 18 hrs. Then the autoclave was cooled to room temperature and the pressure in the autoclave dropped to atmospheric pressure. The reaction product was treated with HCl and washed with water. 0.10 g of black powder was obtained.

X-ray diffraction pattern and Raman spectrum of the sample were measured and the obtained sample was proved to be a mixture of diamond and graphite.

The mixed powder obtained was intensively heat treated with perchloric acid and a diamond granule with average diameter of 270 μ m (determined by SEM) was obtained.

If potassium of the present example was replaced by Li, Na, Rb, Cs as the reducing metal, mixture of diamond and graphite was similarly obtained.

If $MgCO_3$ of the present example was replaced by $CaCO_3$, $CdCO_3$, $CoCO_3$, $CuCO_3$, $FeCO_3$, $BaCO_3$, $MnCO_3$, $NiCO_3$, $PbCO_3$, $SrCO_3$, $ZnCO_3$, Na_2CO_3, K_2CO_3, Li_2CO_3 and the temperature was changed to 950℃, 500℃, 450℃, 480℃, 520℃, 1000℃, 460℃, 550℃, 540℃, 900℃, 440℃, 1500℃, 1400℃, 750℃ respectively, mixture of diamond and graphite was similarly obtained.

Example 12:

2.2 g of Na of chemical pure grade, 16.0 g of NiC_2O_4 and diamond seed of 300 μ m were put into an autoclave of 12 mL which was heated to 480℃ and to a pressure of 500 –

1000 kbar and this state was maintained for 18 hrs. Then the autoclave was cooled to room temperature and the pressure in the autoclave dropped to atmospheric pressure. The reaction product was treated with HCl and washed with water. 0.26 g of black powder was obtained.

X-ray diffraction pattern and Raman spectrum of the sample were measured and the obtained sample was proved to be a mixture of diamond and graphite.

The mixed powder obtained was intensively heat treated with perchloric acid and pure diamond granule with average diameter of the diamond granule of 360 μ m was obtained.

If Na of the present example was replaced by Li, Na, Rb, Cs as the reducing metal, mixtures of diamond and graphite were similarly obtained.

If NiC_2O_4 of the present example was replaced by CaC_2O_4, CdC_2O_4,, CoC_2O_4,, CuC_2O_4, CrC_2O_4, FeC_2O_4, $K_2C_2O_4$, MnC_2O_4, $La_2(C_2O_4)_3$, $Li_2C_2O_4$, MgC_2O_4, $Na_2C_2O_4$, PbC_2O_4, SrC_2O_4, ZnC_2O_4, mixture of diamond and graphite was similarly obtained. Oxalates that could release CO_2 on decomposition could also be used as the carbon source for producing a diamond.

Example 13:

2.5 g of Mg of chemical pure grade and reaction product of Example 2 (used as a seed) were put into an autoclave. The autoclave was heated to 650℃ and CO_2 gas was fed into autoclave under pressure to 500 – 1500 kbar and this state was maintained for 12 hrs. Then the autoclave was cooled to room temperature and the pressure in the autoclave dropped to atmospheric pressure. The reaction product was treated with HCl and washed with water. 0.24 g of black powder was obtained.

X-ray diffraction pattern and Raman spectrum of the sample were measured and the obtained sample was proved to be a mixture of diamond and graphite.

The mixed powder obtained was intensively heat treated with perchloric acid and pure diamond granule was finally obtained. SEM micrograph indicated that the average diameter of the diamond granule was 3200 μ m.

If Mg in the present example was replaced by Ca, Sr, Ba as the reducing metal and the temperature was changed to 860℃, 840℃, 780℃, mixture of diamond and graphite was similarly obtained.

Example 14:

2.0 g of Sr of chemical pure grade, 8.0 g of self-prepared dry ice and diamond seed of 300 μ m were put into an autoclave of a capacity of 12 mL. The autoclave was heated to 800℃ so that the pressure in the autoclave reached 500 – 1000 kbar and this state was maintained for 16 hrs. Then the autoclave was cooled to room temperature and the pressure in the autoclave dropped to atmospheric pressure. The reaction product was treated with HCl and washed with water. 0.21 g of black powder was obtained.

X-ray diffraction pattern and Raman spectrum of the sample were measured and the obtained sample was proved to be a mixture of diamond and graphite.

The mixed powder obtained was intensively heat treated with perchloric acid and pure diamond granule was finally obtained. SEM micrograph indicated that the average diameter of the diamond granule was 1100 μ m.

If Sr of the present example was replaced by Ca, Mg, Ba as the reducing metal and

temperature was changed to 880℃, 680℃ and 820℃ respectively, mixtures of diamond and graphite were similarly obtained.

Example 15:

2.0 g of Mg of chemical pure grade, 14.0 g of FeC_2O_4 and diamond seed of 300 μ m were put into an autoclave of 12 mL which was heated to 700℃ and to a pressure of 500 – 1000 kbar and this state was maintained for 16 hrs. Then the autoclave was cooled to room temperature and the pressure in the autoclave dropped to atmospheric pressure. The reaction product was treated with HCl and washed with water. 0.20 g of black powder was obtained.

X-ray diffraction pattern and Raman spectrum of the sample were measured and the obtained sample was proved to be a mixture of diamond and graphite.

The mixed powder obtained was intensively heat treated with perchloric acid and pure diamond granule with average diameter of 800 μ m was obtained.

If Mg of the present example was replaced by Ca, Sr, Ba as the reducing metal and the temperature was changed to 860℃, 840℃, 780℃, mixture of diamond and graphite was similarly obtained.

If FeC_2O_4 of the present example was replaced by CaC_2O_4, CdC_2O_4, CoC_2O_4, CuC_2O_4, CrC_2O_4, NiC_2O_4, $K_2C_2O_4$, MnC_2O_4, $La_2(C_2O_4)_3$, $Li_2C_2O_4$, MgC_2O_4, $Na_2C_2O_4$, PbC_2O_4, SrC_2O_4, ZnC_2O_4, mixture of diamond and graphite was similarly obtained.

Example 16:

2.0 g of Ca of chemical pure grade, 16.0 g of $FeCO_3$ and diamond seed of 300 μ m were put into an autoclave of 12 mL which was heated to 850℃ and to a pressure of 500 – 1000 kbar and this state was maintained for 16 hrs. Then the autoclave was cooled to room temperature and the pressure in the autoclave dropped to atmospheric pressure. The reaction product was treated with HCl and washed with water. 0.20 g of black powder was obtained.

X-ray diffraction pattern and Raman spectrum of the sample were measured and the obtained sample was proved to be a mixture of diamond and graphite.

The mixed powder obtained was intensively heat treated with perchloric acid and pure diamond granule with an average diameter of 1600 μ m (determined by SEM) was obtained.

If Ca of the present example was replaced by Mg, Sr, Ba as the reducing metal and the temperature was changed to 660℃, 880℃, 820℃, mixtures of diamond and graphite were similarly obtained.

If $FeCO_3$ of the present example was replaced by $CaCO_3$, $CdCO_3$, $CoCO_3$, $CuCO_3$, $MgCO_3$, $BaCO_3$, $MnCO_3$, $NiCO_3$, $PbCO_3$, $SrCO_3$, $ZnCO_3$, Na_2CO_3, K_2CO_3, Li_2CO_3 and the temperature was changed to 950℃, 860℃, 870℃, 880℃, 920℃, 1000℃, 860℃, 950℃, 850℃, 900℃, 880℃, 1500℃, 1400℃, 850℃, respectively, mixture of diamond and graphite was similarly obtained.